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(19) (11) Publication number: 0 335 382 A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 89105572.5

(22) Date of filing: 29.03.89

(51) Int. Cl.4: H01B 1/06 , C04B 35/58 , F23Q 7/00

(30) Priority: 29.03.88 JP 75551/88

(43) Date of publication of application: 04.10.89 Bulletin 89/40

(84) Designated Contracting States: DE FR GB

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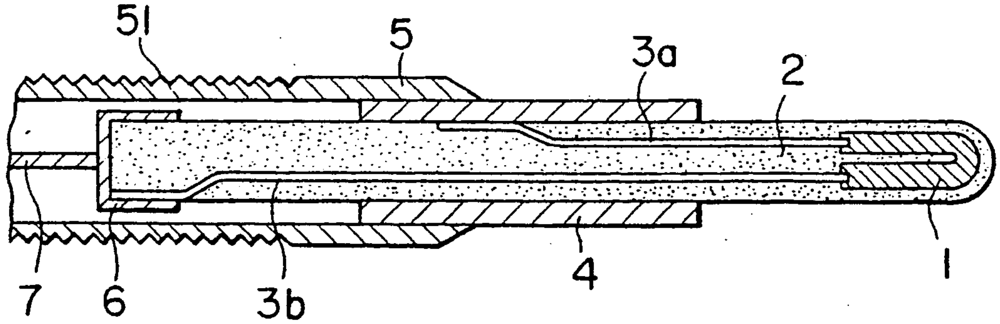
(54) **Electrically conductive ceramic material.**

(57) An electrically conductive ceramic material containing at least Mo_5Si_3C is disclosed. Furthermore, a self-controlling type glow plug is disclosed wherein a resistor for controlling supply of electric current to a heating element is connected in series to the heating element. This self-controlling type glow plug comprises an electrically conductive ceramic material for the heating element containing at least Mo_5Si_3C and a material for the resistor having a larger resistance-temperature coefficient than that of the heating element.

FIG. 1



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ELECTRICALLY CONDUCTIVE CERAMIC MATERIAL

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a ceramic material with a small resistance-temperature coefficient, and, more particularly, to a ceramic material which can be effectively used to serve as the heating element of a self-controlling type glow plug.

DESCRIPTION OF THE RELATED ART

Hitherto, ceramic heating elements have been prepared by combining and dispersing electrically conductive ceramics such as TiN and $MoSi_2$ and insulating type ceramics such as Si_3N_4 and sintering these combined ceramics.

However, a sufficiently reduced resistance-temperature coefficient could not be obtained in a ceramic heating element of such a type as described above, because attempts to reduce the resistance-temperature coefficient meet inherent limitations due to usual influence of the specific temperature-resistance coefficient of electrically conductive ceramics such as TiN and $MoSi_2$.

For example, in a known self-controlling type glow plug provided with the above-described type ceramic heating element and a resistor for controlling electric current connected in series to said element.

Since the resistance-temperature coefficient of the element cannot be sufficiently reduced, the heating element itself acts as the resistor when the temperature of the heating element is raised, the amount of electric current to be supplied to the heating element cannot be controlled properly with the resistor for controlling electric current, and satisfactory temperature-rising characteristics cannot be obtained.

SUMMARY OF THE INVENTION

An object of the presnt invention is to provide an electrically conductive ceramic material of an extremely reduced resistance-temperature coefficient, and as well to obtain a self-controlling type glow plug exhibiting excellent temperature-rising characteristics.

According to the present invention, a self-controlling type glow plug is provided wherein a resistor for controlling the supply of electric current to a heating element is connected in series to the heating element, the self-controlling type glow plug comprising an electrically conductive ceramic material at least containing Mo_5Si_3C, and a material for the resistor having a larger resistance-temperature coefficient than that of the heating element.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view illustrating a glow plug according to one embodiment of the present invention.

Fig. 2 is a graph showing the electricity supplying characteristics of the glow plug of Fig. 1.

Fig. 3 is a cross-sectional view illustrating another glow plug according to the present invention.

Fig. 4 is a graph illustraing the temperature-rising characteristics of the glow plug of Fig. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Since Mo_5Si_3 proposed as the conventional electrically conductive ceramic material contains an excessive amount of Mo atoms, its resistance-temperature coefficient cannot be sufficiently reduced. Furthermore, since $MoSi_2$ contains an excessive amount of Si atoms in which the ratio of Mo atoms is smaller than in Mo_5Si_3, the resistance-temperature coefficient cannot be reduced sufficiently.

The present inventors have found that Mo_5Si_3C can serve as a ceramic material exhibiting a sufficiently

reduced resistance-temperature coefficient.

The present invention employs Mo_5Si_3C as electrically conductive ceramic material wherein Mo_5Si_3C can be expressed more accurately by the formula $Mo_{5-X}Si_3C_{1-Y}$ ($0 \leqq X \leqq 2$, $0 \leqq Y < 1$). The reason why X is 2 or less lies in that the two atoms of the five Mo atoms can easily give rise to lattice defects. Furthermore, the reason why Y is smaller than 1 also lies in that C atom can easily give rise to lattice defects. Since the normal case in which no lattice defects are generated can be realized with a composition expressed by Mo_5Si_3C, the "Mo_5Si_3C" will be used hereinafter for the above-described formula.

A sufficiently reduced resistance-temperature coefficient can be obtained with Mo_5Si_3C since the content of Mo atoms in Mo_5Si_3C is smaller than that in Mo_5Si_3, that is, the content of Mo atoms is not excessive, and the content of Si atoms in Mo_5Si_3C is smaller than that in $MoSi_2$, that is, the content of the Si atoms is not excessive.

Furthermore, a self-controlling type glow plug exhibiting an excellent temperature-rising characteristics can be obtained by using this ceramic material as the heating element. That is, the resistance can be made sufficiently larger than the resistance of the resistor at the initial stage of the electricity supply to the glow plug. On the other hand, the resistance of the heating element can be made smaller than the resistance of the resistor at the time when the electricity supply to the same is controlled, causing the heating rate of the heating element to be increased and an excessive rise in the temperature of this heating element to be prevented.

Example 1

A method of preparing Mo_5Si_3C will now be described.

As shown in Table 1, 0.5 to 3.0 wt% of carbon black was added to Mo_5Si_3 powder having a mean particle size of 1 μm, and then they were mixed and pulverized in a ball mill. The thus-obtained material was burned in a hot press at 1700 °C for 60 minutes under a pressure of 300 kg/cm^2 in an atmosphere of Ar at 1 atm. Thus, a ceramic body was prepared. The obtained ceramic bodies with the compositions of Mo_5Si_3C of samples 1 to 6 were heated up to 900 °C under vacuum. Then, the volume resistivity of each of the samples was obtained by a 4-terminal method, and the change rate with respect to the volume resistivity at room temperature was obtained.

The results are shown in Table 1. In addition, the results of some samples obtained by burning $MoSi_2$, TiN, and Mo_5Si_3 under the same conditions are also shown in Table 1 as comparative examples.

Table 1

		Amount of carbon black added (wt%)	Resistance-temperature coefficient (x $10^{-4}deg^{-1}$)
Sample	1	0.5	10.3
	2	1.0	7.10
	3	1.5	4.80
	4	2.0	3.21
	5	2.5	3.44
	6	3.0	3.38
Comparative Example	1	$MoSi_2$	64.2
	2	TiN	25.3
	3	Mo_5Si_3	14.1

As is seen from Table 1, as the quantity of the carbon black added to Mo_5Si_3 increases, a quantity of Mo_5Si_3C having the completely different structure-from Mo_5Si_3 increases in addition to Mo_5Si_3 in the burned ceramic. As a result, a further smaller resistance-temperature coefficient than the smallest resistance-temperature coefficient ever realized by the Mo_5Si_3 conventionally used was obtained. Furthermore, when the carbon black was added in a quantity exceeding 2.0 wt%, Mo_5Si_3 was substantially converted to Mo_5Si_3C, causing a satisfactory stable resistance-temperature coefficient. The thus obtained stable resistance-temperature coefficient of the electrically conductive ceramic material had a sufficiently reduced value which was substantially 1/5 to 1/20 of the resistance-temperature coefficient obtained by the electrically conductive ceramic materials according to the Comparative Examples 1 to 3.

Although Mo_5Si_3C was obtained by adding carbon black to the starting material Mo_5Si_3 in the embodiment above, the present invention should not be limited to this embodiment. For example, a similar effect can be obtained from a material obtained by mixing Mo fine particles, Si fine particles, and carbon fine particles at a predetermined proportion.

Example 2

Next, a ceramic heater was manufactured by using the electrically conductive ceramic Mo_5Si_3C.

In order to realize the atomic ratio of Mo:Si:C = 5:3:1, Mo_5Si_3 having a mean particle size of 1 μm and carbon black were mixed, and the thus mixed powder and Si_3N_4 having a mean particle size of 10 μm or 1 μm were mixed in order to realize Si_3N_4:Mo_5Si_3C = 20 to 80:80 to 20. Then, the material to which each 5 wt% of Y_2O_3 and Al_2O_3 were added as a burning aid was wet-mixed for 12 hours in a ball mill. As a solvent, ethanol was used. The thus mixed powder was burned in a hot-press at 1700°C for 60 minutes under a pressure of 300 kg/cm^2 and in an atmosphere of Ar at 1 atm.

The thus obtained samples 7 to 17 were subjected to measurements of resistivity and change rate of resistance as shown in Example 1. The results are shown in Table 2. In addition, the bending strength σ of these samples is also shown.

Table 2

		Composition	Mean particle size of Si_3N_4	Resistivity ($\Omega \cdot cm$)	Resistance-temperature coefficient ($\times 10^{-4} deg^{-1}$)	σ (kg/ml)
Sample	7	Si_3N_4-80Mo_5Si_3C	D_{50} = 1 μm	8.7×10^{-4}	1.19	25
	8	Si_3N_4-70Mo_5Si_3C	D_{50} = 1 μm	2.2×10^{-3}	1.22	37
	9	Si_3N_4-60Mo_5Si_3C	D_{50} = 1 μm	1.3×10^{-2}	1.24	44
	10	Si_3N_4-50Mo_5Si_3C	D_{50} = 10 μm	3.1×10^{-4}	1.29	55
	11	Si_3N_4-40Mo_5Si_3C	D_{50} = 10 μm	9.6×10^{-4}	1.31	67
	12	Si_3N_4-30Mo_5Si_3C	D_{50} = 10 μm	3.2×10^{-3}	1.24	75
	13	Si_3N_4-20Mo_5Si_3C	D_{50} = 10 μm	2.3×10^{-1}	1.21	78
Comparative Example	4	Si_3N_4-30$MoSi_2$	D_{50} = 10 μm	2.5×10^{-2}	30.02	77
	5	Si_3N_4-70$MoSi_2$	D_{50} = 1 μm	1.9×10^{-3}	10.50	46

Furthermore, the characteristics of the ceramic heaters formed by Si_3N_4 and $MoSi_2$ are respectively shown as Comparative Examples 4 to 5.

As is seen from Table 2, a sufficiently reduced resistance-temperature coefficient of 5.0×10^{-4} deg^{-1} or less was realized in the electrically conductive ceramic material with respect to the case where $MoSi_2$ was used by dispersing Mo_5Si_3C serving as the electrically conductive ceramic material in Si_3N_4 serving as the insulating ceramic material and by simultaneously burning the thus dispersed materials. Furthermore,

ceramics for a heater having a desired resistivity with the thus realized low resistance-temperature coefficient maintained was obtained.

Although Si_3N_4 was used as the insulating ceramic material, the present invention should not be limited to the example above. All materials having an insulating property may be used in the present invention. Therefore, for example, Al_2O_3, AlN, and ZrO_2 can realize the similar effects.

Example 3

Fig. 1 is a cross-sectional view illustrating a glow plug in which the electrically conductive ceramic material according to the present invention is employed.

As shown in Fig. 1, this glow plug has such a structure that heater 1 of a U-shaped cross section is formed within the end of support member 2 having a circular cross-sectional shape. Furthermore, the support member 2 is provided with electrically conductive wires 3a and 3b of tungsten embedded therein, of which the ends are connected to the heater 1. Metallic pipe 4 is attached around the support member 2, and the end of metallic housing 5 in a cylinder form is connected to the metallic pipe 4. The other end of the electrically conductive wire 3a extends to the base portion of the support member 2 and is connected to metallic cap 6 installed around this base portion, so that the electrically conductive wire 3a is connected to a power source (omitted from illustration) via this metallic cap 6 and nickel wire 7. On the other hand, the other end of the electrically conductive wire 3b is connected to a metallic sleeve.

The support member 2 and the metallic pipe 4 were coupled by applying nickel plating to the surface thereof and performing blazing of the plated surface. The pipe 4 and the housing 5 were coupled by blazing.

The composition of the material for the heater 1 consisted of 70 wt% of Si_3N_4 having a mean particle size of 10 μm and 30 wt% of Mo_5Si_3C having a mean particle size of 1 μm. The composition of the material for the support member 2 consisted of 72 wt% of Si_3N_4 having a mean particle size of 1 μm and 28 wt% of $MoSi_2$ having a mean particle size of 1 μm. As a burning aid, Y_2O_3 and Al_2O_3 were added in each amount of 5%. In this example, the composition of the material for the support member 2 was arranged in such a manner that the thermal expansion coefficient of the material of the support member 2 and that of the heater 1 became the same.

By virtue of employment of an Si_3N_4 powder having a mean particle size of 10 μm for the material of the heater 1, Mo_5Si_3C particles surrounded the Si_3N_4 particles, so that the Mo_5Si_3C particles were provided in a continuous manner as electrically conductive structure. Furthermore, by virtue of employment of Si_3N_4 particles having a mean particle size of 1 μm as the material for the support member 2, the electrically conductive $MoSi_2$ particles were surrounded by the insulating Si_3N_4 particles, so that the former were separated from one another. As a result, an electrically insulated structure was formed.

The reason why Si_3N_4 having a mean particle size of 10 μm was used as the material of the heater 1 lies in that reduction in coefficient of thermal expansion and improvement in bending strength are intended by reducing, as described in Example 2, the quantity of Mo_5Si_3C which needs to be provided for the purpose of obtaining the desired resistivity.

The reason why the $MoSi_2$ particles are dispersed in the material for the support member 2 lies in that the thermal stress which will be generated between the material for the heater 1 and that for this support member 2 is intended to be reduced by making its coefficient of thermal expansion equal to that of the material of the heater 1.

Fig. 2 is a graph which illustrates an electric supplying characteristics of this ceramic heater.

As is seen from Fig. 2, since the heater 1 containing Mo_5Si_3C was used, excellent characteristics for a constant electricity consumption type glow plug could be obtained having a satisfactory reduced resistance-temperature coefficient realized in the material for the heater 1.

The structure of the glow plug is not limited to that employed in this example. Any ceramic heaters containing at least electrically conductive ceramic material Mo_5Si_3C may be employed.

Although the ceramic heater can be obtained by mixing the electrically conductive ceramic material comprising Mo_5Si_3C and the insulating ceramic material, the electrically conductive ceramic material according to the present invention can be used for many other-purposes, for example, it may be used in a resistor employed as a multilayered substrate or in wiring on substrates.

Example 4

The self-controlling type glow plug according to the present invention is schematically shown in Fig. 3. To the components in Fig. 2 are given the same reference numerals as shown in Fig. 1.

Reference numeral 10 represents a ceramic element. The ceramic element 10 is structured in such a manner that heater 1 serving as the heating portion and electrodes 3a and 3b are formed therein, as shown in Eaxmple 3.

The electrode 3a disposed within this ceramic element 10 is electrically connected to housing 5 via sleeve 4. On the other hand, the electrode 3b is electrically connected to second resistor 15 via cap 6 and lead wire 7. The other end of the resistor 15 is connected to electrode 8. This resistor 15 is made of a material with a larger resistance-temperature coefficient than that of the heater 1, for example, it is made of Fe or Ni.

Then, the operation of this self-controlling type glow plug will be described with reference to Fig. 4.

When the self-controlling type glow plug according to this example is heated by applying an electricity thereto, the temperature of the heater 1 is rapidly raised at the initial stage of the electricity supply since the resistance of the heater 1 is sufficiently larger than that of the resistor 15. However, as is seen from Fig. 4, the resistance of the resistor 15 becomes, in 40 seconds after the start of electricity supply, sufficiently larger than that of the heater 1, and an excessive supply of electricity to the heater 1 is prevented and the overheat of the heater 1 can be effectively prevented.

Furthermore, the R.T. coefficient (ratio of a resistance at 900° C and that at 20° C) of the heating portion of the self-controlling type glow plug according to this example can be improved to be substantially 1.20, as compared with substantially 1.69 achieved by a glow plug in which a metallic heating element (tungsten-rhenium) is embedded therein. Therefore, a self-controlling type glow plug exhibiting an excellent temperature-rising characteristics is obtained, whereby time taken for the heating portion to rise to 900° C is significantly shorted from conventional value of 4.0 seconds to 3.0 seconds.

According to the present invention, a ceramic material exhibiting a sufficiently reduced resistance-temperature coefficient can be obtained by using Mo_5Si_3C as the electrically conductive ceramic material.

Furthermore, a self-controlling type glow plug structured by a heating portion and a control portion made of a material with a larger resistance-temperature coefficient than that of the material for the heating portion can be made a self-controlling type glow plug exhibiting an excellent temperature-rising characteristics since the heating portion thereof is made of an electrically conductive ceramic material containing Mo_5Si_3C of which the resistance-temperature coefficient is sufficiently reduced.

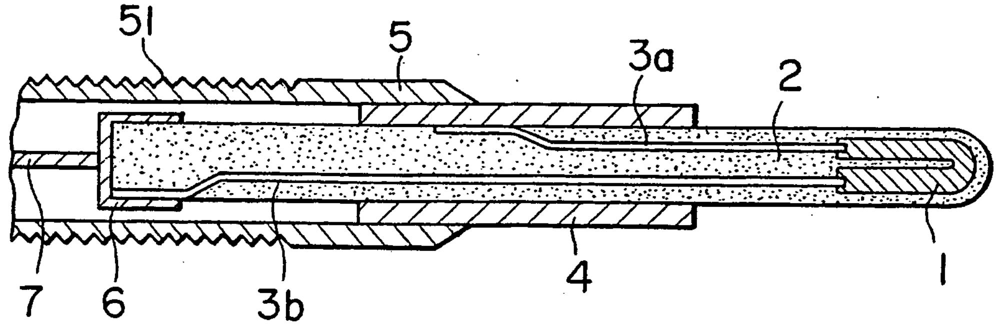
Claims

1. An electrically conductive ceramic material containing at least Mo_5Si_3C.

2. An electrically conductive ceramic material containing Mo_5Si_3C and having a resistance-temperature coefficient of 5×10^{-4} deg^{-1} or less.

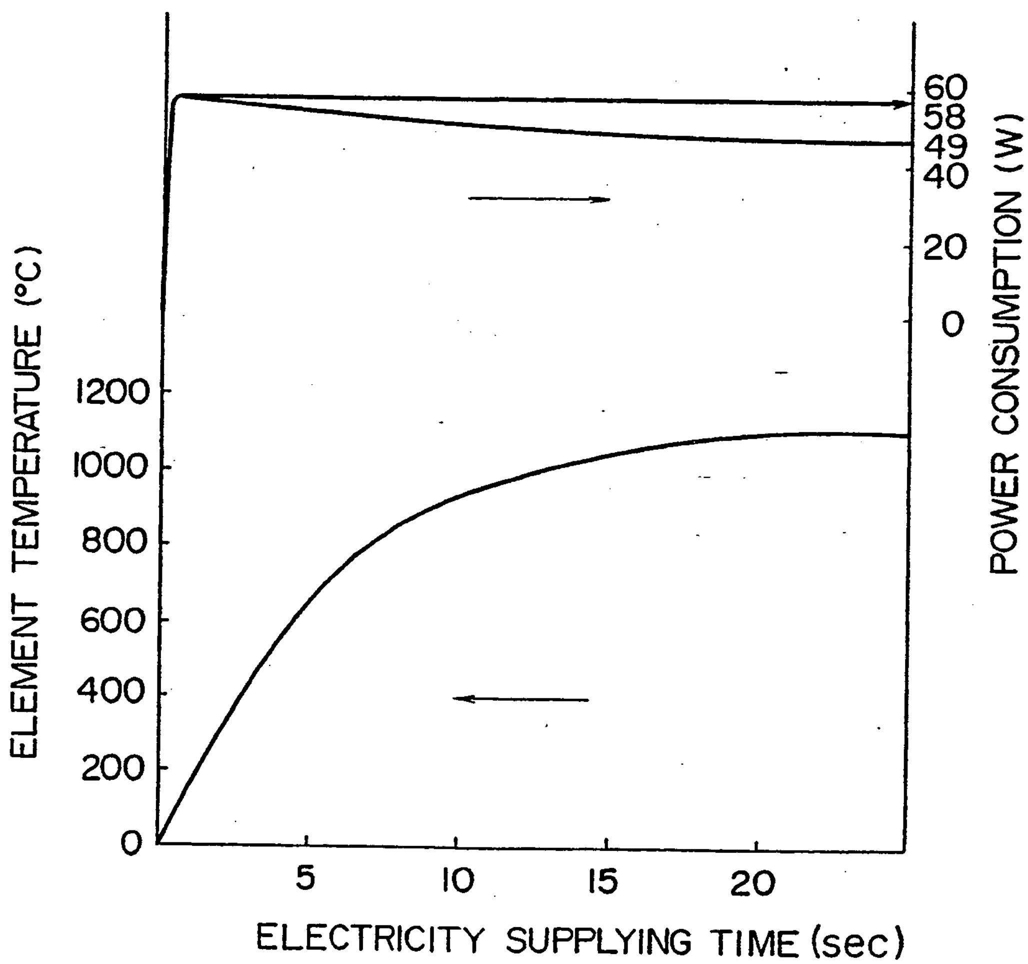
3. A self-controlling type glow plug wherein a resistor for controlling supply of electric current to a heating element is connected in series to said heating element, said self-controlling type glow plug comprising an electrically conductive ceramic material for said heating element containing at least Mo_5Si_3C; and
a material for said resistor having a larger resistance-temperature coefficient than that of said heating element.

F I G. 1



51
5
3a
2
7
6
3b
4
1

F I G. 2



ELEMENT TEMPERATURE (°C)
0
200
400
600
800
1000
1200
POWER CONSUMPTION (W)
0
20
40
49
58
60
5
10
15
20
ELECTRICITY SUPPLYING TIME (sec)

FIG. 3

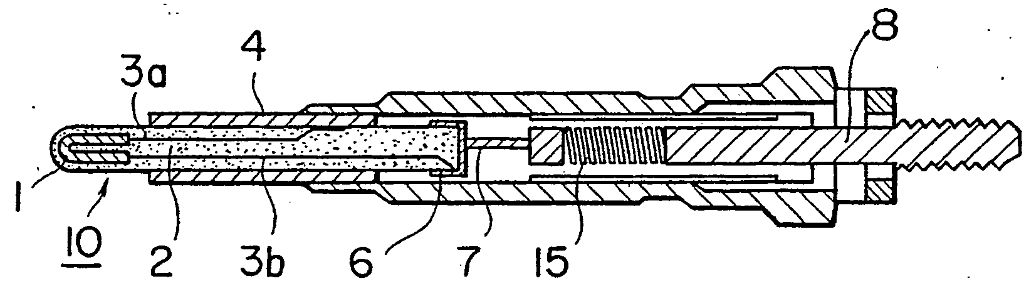
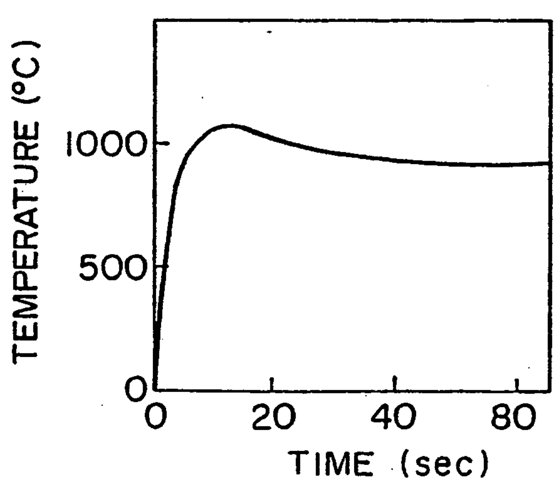


FIG. 4



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EUROPEAN SEARCH REPORT

Application number

EP 89105572.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US - A - 4 634 837 (ITO et al.) * Abstract; fig. 1 * --	1-3	H 01 B 1/06 C 04 B 35/58 F 23 Q 7/00
A	PROC. OF THE 10th PLANSEE--SEMINAR 1981, vol. 1, Ed. H. M. Ortner, Metallwerk Plansee, Reutte, Austria VAN LOO et al. "Phase Relations and Diffusion Paths in the Mo-Si-C System at 1200°C" * Page 146, table I; fig. 3 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

H 01 B 1/00
C 04 B 35/00
F 23 Q 7/00
H 05 B 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	16-06-1989	KUTZELNIGG

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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